

FINAL REPORT
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Name of the Principal Investigator: Melinda D. Dyar

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Name and address of recipient's institution: Mount Holyoke College
50 College St.
South Hadley, MA 01075

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PROPOSAL SUMMARY (ABSTRACT)

Knowledge of oxygen and hydrogen fugacity is of paramount importance in constraining phase equilibria and crystallization processes of melts, as well as understanding the partitioning of elements between the core and silicate portions of terrestrial planets. H and Fe^{3+} must both be analyzed in order to reconstruct hydrogen and oxygen fugacities on Mars. To date, SIMS data have elucidated D/H and H contents of hydrous phases in SNC meteorites, but until now anhydrous martian minerals have not been systematically examined for trace hydrogen. Ferric iron has been quantified using XANES in many martian phases, but integrated studies of both Fe^{3+} and H on the same spots are really needed to address the H budget. Finally, the effects of shock on both Fe^{3+} and H in hydrous and anhydrous phases must be quantified.

Thus, the overall goal of this research was to understand the oxygen and hydrogen fugacities under which martian samples crystallized. In this research one-year project, we approached this problem by 1) characterizing Fe^{3+} and H contents of SNC meteorites using both bulk (Mössbauer spectroscopy and uranium extraction, respectively) and microscale (synchrotron micro-XANES and SIMS) methods; 2) relating Fe^{3+} and H contents of martian minerals to their oxygen and hydrogen fugacities through analysis of experimentally equilibrated phases (for pyroxene) and through study of volcanic rocks in which the oxygen and hydrogen fugacities can be independently constrained (for feldspar); and 3) studying the effects of shock processes on Fe^{3+} and H contents of the phases of interest. Results have been used to assess quantitatively the distribution of H and Fe^{3+} among phases in the martian interior, which will better constrain the geodynamic processes of the interior, as well as the overall hydrogen and water budgets on Mars. There were no inventions funded by this research.

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SUMMARY OF RESEARCH

Task 1. Obtain transmission FTIR measurements to quantify H in nominally anhydrous minerals in meteorites

During the funded period, we engaged in extensive cautious analytical work dedicated to developing the methods used for analysis of H in anhydrous minerals from SNC meteorites. We initially obtained thin billets of both Nakhla (from JSC) and Chassigny (from the Vatican Observatory) and prepared free-standing 100 μm "thick sections" from them. To our great disappointment, both sections had previously been impregnated with epoxy, and the epoxy bands contaminated the OH region of interest ($\sim 3600\text{ cm}^{-1}$) for all the grains we studied. Over six months of measurements on the synchrotron micro-FTIR at Brookhaven, we finished mapping the band intensity in several regions on each section, only to see repeated evidence of epoxy contamination. To test our sample preparation procedures, we also prepared mounts of analogous lithologies from mantle xenoliths and basalts, and obtained beautiful OH spectra from olivines, pyroxenes, feldspars, and melts in them. Thus, we learned that although the FTIR-standard method for sample preparation works for terrestrial samples, the fracture histories of the meteorites permit epoxy to penetrate microfractures, from which it is exceedingly difficult to remove. So we learned that we cannot study our samples in thick sections, with petrographic context, but relied instead on analyses of single crystals prepared using soluble adhesives (such as Crystal Bond) or acrylic plastics. Even still, it is difficult to completely eliminate organic residues.

Thus, we prepared about 50 single crystals extracted from SNC meteorites in the requisite geometry of doubly-polished, 40-50 μm -thick individual mineral grains supported on the edges by Crystal Bond adhesive. We acquired transmission FTIR spectra of these samples (Figure 1), which show the presence of significant ($>1000\text{ ppm H}_2\text{O}$) in both pyroxenes and olivines. All the crystals were randomly oriented, so precise quantification of H contents (which must be made with the beam polarized along specific optical orientations) was not possible. However, significant water bands are present in olivine and pyroxene crystals extracted from SNC meteorites. The presence of distinct absorption bands within the broad O-H absorbance argues for some component of hydrous defects rather than water on surfaces or in inclusions. These results were reported in Dyar et al. (2004); a full manuscript is now being prepared.

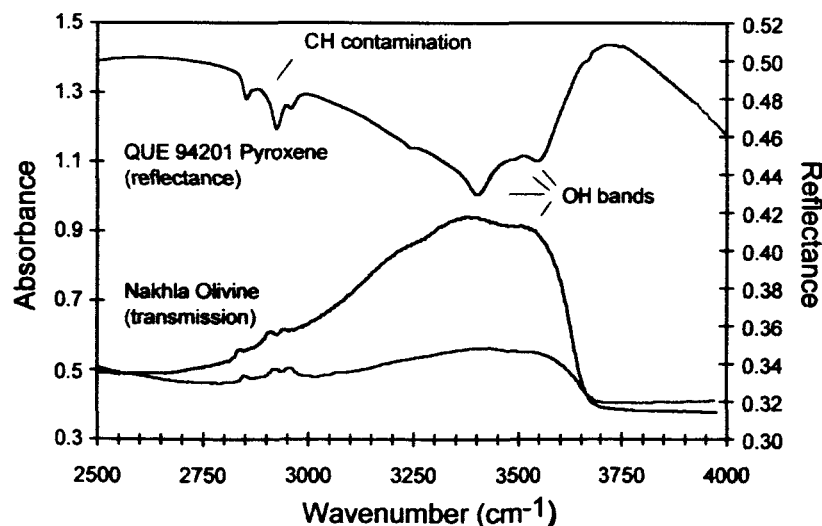


Figure 1. Reflectance (red line) and transmission spectra (blue lines) of OH in minerals from SNC meteorites. Reflectance spectra were taken from powders made from hand-picked mineral separates. Transmission spectra were acquired on doubly polished 40 μm thick single crystals. From Dyar et al., in preparation.

Task 2. Measure Fe^{3+} contents of mineral separates from extraterrestrial samples using Mössbauer spectroscopy

We created mineral separates of Fe-bearing phases in ten of the SNC meteorites and acquired Mössbauer spectra first of the whole rocks and then of the separates made from them (e.g., Figure 2). Results were presented at the Un-Mixing the SNC's meeting in October 2002 (Dyar, 2002) and at LPSC (Dyar, 2003a), and published in the MAPS special issue on SNC meteorites (Dyar, 2003b). All of the samples studied have less than 8% of the total Fe as Fe^{3+} , and the results for individual meteorites agree well with the most recent XANES measurements of these same samples. We found no relationship between Fe^{3+} content and f_{O_2} as calculated by independent methods. This strongly suggests that all of the Fe^{3+} observed in olivine is the result of dehydrogenation rather than oxidation; this process may also be the source of all the Fe^{3+} observed in pyroxene. It is equally likely that the observed Fe^{3+} in pyroxene records an equilibrium between pyroxene and melt at such low f_{O_2} 's that little or no Fe^{3+} would be expected.

Our other Mössbauer work focused on the study of lunar feldspars (Therkelsen et al., 2002; Dyar et al., 2002; Delaney et al., 2003). Because Fe behaves like a trace element in feldspar, determination of the Fe site distributions and valence states of Fe in feldspars provides especially useful insights into the composition and oxidation state of the parent magmas and the thermal histories of the host rocks. However, few such studies exist for samples with petrologically well-constrained petrogeneses, such as those from lunar rocks. We have undertaken a study of a good terrestrial analog, the Skaergaard Complex, and those results are reported in Tegner et al. (2003); related studies of terrestrial feldspars in rhyolitic magmas were reported in Seaman et al. (2003).

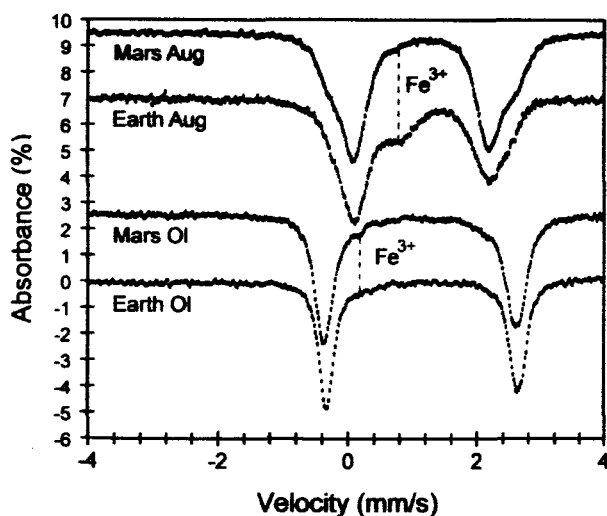


Figure 2. Comparison of Mössbauer spectra of terrestrial augite and pyroxene vs. the same minerals from the Nakhla (Mars) meteorite. On Earth, the most oxidized magmatic or mantle olivines contain roughly 7% of the total Fe as Fe^{3+} ; on Mars, the range is 0-8% also. However, on Earth the oxidized olivines are in equilibrium with pyroxenes that are 30-50% Fe^{3+} . On Mars, the most oxidized pyroxenes are only ~8% Fe^{3+} . These data suggest that the source regions for Mars meteorites are reduced relative to those on Earth, and also raise the possibility that some or all of the Fe^{3+} observed was actually H pre-shock or eruption, and the H has subsequently dehydrogenated. Results from Dyar (2003).

Many young planetary scientists are not aware of the fact that Fe^{3+} in lunar feldspar was reported by numerous investigators, though this work was controversial even at that time because all the other lunar phases were completely reduced. Feldspar in Apollo 11 and 12 was studied by Hafner et al. (1971), who assigned two Fe^{3+} doublets to tetrahedral and octahedral coordination. Fe^{3+} was also reported in Apollo 14 feldspar (Finger et al., 1972 and Schürmann and Hafner, 1972); up to 10% of the total Fe atoms were Fe^{3+} but linewidths were broad and the statistics on the data were poor. Similar site assignments were reached by Appleman et al. (1971), though they did not detect any Fe^{3+} . In short, the controversy could not be resolved because a) the existing Mössbauer instruments were inadequate for detection of such low Fe concentrations, and b) data were needed on ^{57}Fe -doped synthetic feldspars to establish standard parameters for Fe^{3+} in the feldspar structure. The first of these problems would wait 30 years to be solved by better technology; the spectrometer in the P.I.'s lab is a state of the art instrument

designed for small samples sizes and low Fe samples. So it is now possible to obtain excellent signal to noise ratios in spectra of feldspars. The needed synthetic feldspars were, in fact, synthesized in 1972 by Robert Housely, but the main lunar sample study program took a different direction and nothing was published concerning his work. In 2001 we obtained the pair of synthetic samples from Housely and collaborated with him on a study of their Mössbauer parameters (Dyar et al., 2002). We now have all the background information needed to revisit the issue of Fe^{3+} in lunar feldspars.

Task 3. Integrate our FTIR and Mössbauer Results with other Spectroscopic Results

While we were in the process of preparing bulk mineral separates for Mössbauer analysis of phases in SNC meteorites, it became apparent that it would be useful to obtain reflectance spectra of the separates before they were diluted with sugar. The results (Figure 3) turned out to be highly interesting. As expected, Mars pyroxenes and olivine are readily identified from the near-IR data. The distinct Fe^{+2} electronic transition bands of pyroxene occur near 1 and 2 μm , and the composite band of Chassigny olivine centered near 1.05 μm consists of three superimposed Fe^{+2} electronic transition bands. All spectra agree well with comparable minerals that have been studied and found in the literature. The near-IR spectra of these four Mars pyroxene separates exhibit the well-known trend of electronic transition Fe^{+2} bands that shift to longer wavelengths as Fe and Ca substitute for Mg in the pyroxene structure.

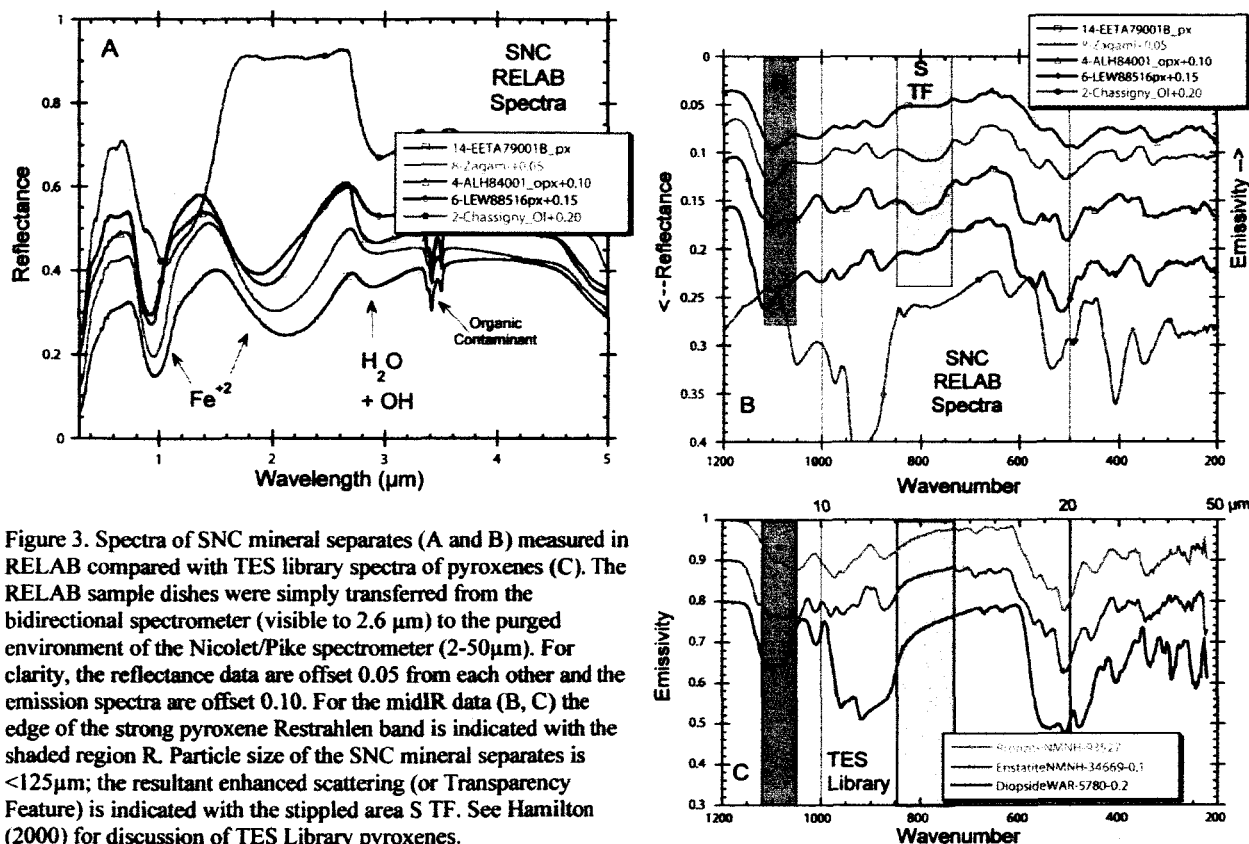


Figure 3. Spectra of SNC mineral separates (A and B) measured in RELAB compared with TES library spectra of pyroxenes (C). The RELAB sample dishes were simply transferred from the bidirectional spectrometer (visible to 2.6 μm) to the purged environment of the Nicolet/Pike spectrometer (2-50 μm). For clarity, the reflectance data are offset 0.05 from each other and the emission spectra are offset 0.10. For the midIR data (B, C) the edge of the strong pyroxene Reststrahlen band is indicated with the shaded region R. Particle size of the SNC mineral separates is $<125\mu\text{m}$; the resultant enhanced scattering (or Transparency Feature) is indicated with the stippled area S TF. See Hamilton (2000) for discussion of TES Library pyroxenes.

The data in Figure 3 also provide an example of why it is so important to carry out integrated analyses (Mössbauer, nearIR, midIR spectroscopy) with Mars-specific materials. Note the similarity of the spectra for Chassigny olivine and LEW88516 pyroxene between 500 and 200 wavenumbers (20-50 μm). The olivine features in this part of the spectrum were believed to be unique based on library data in hand and have tentatively been used to map olivine content on Mars from TES data (Hoefen and Clark, 2001). However, the Mössbauer data tell us that the LEW88516 pyroxene separate is pure and contains

only a low-Ca pyroxene (see short wavelength bands in the near-IR data of Fig 3A). It appears that an *actual* Mars low-Ca pyroxene (perhaps pigeonite) can masquerade as olivine at these long wavelengths. (Pigeonite is an example of a mineral that has been difficult to obtain for spectral libraries; c.f. Hamilton, 2000.) Reflectance data from SNC meteorites were reported in Pieters et al. (2004) and Sunshine et al. (2004), and a full-length manuscript is being prepared at this writing.

Task 4. Measure Fe^{3+} contents of minerals in thin section from SNC meteorites using synchrotron micro-XANES spectroscopy

Although the Mössbauer measurements can provide excellent bulk Fe^{3+} contents for Fe-rich phases of interest, *microanalysis* of Fe^{3+} remains a major priority because of the potential for analyzing tiny samples and for recognizing microscale variations in Fe valence state such as zoning due to changes in melt composition during crystallization. To this end, we have collected over 400 micro-XANES analyses of phases in SNC meteorites that have been reported in a series of abstracts by Delaney et al. (1999a, b; 2000), Delaney and Dyar (2001, 2002, 2003) and Dyar et al. (1999; 2000a, b; 2001a).

As was formerly the case with the Mössbauer data, the micro-XANES results cannot be confidently published until the analytical problems associated with the technique have been properly dealt with. Thus, we were unavoidably occupied with technique development during this funding period. Three primary issues had to be considered: 1) selection and characterization of Fe^{2+} and Fe^{3+} end-member standards for each mineral group of interest, 2) The proper interpretation of the pre-edge features in spectra of each mineral group, and 3) the effect of orientation on pre-edge spectra.

1. The task of selecting Fe^{2+} and Fe^{3+} end-members for relevant mineral groups was straightforward because this P.I. already had >4,000 minerals for which Mössbauer spectra had already been acquired in her collections. Thus, we have developed several mineral group-specific calibration lines. These calibrations express the relationship between the centroid of the XANES pre-edge region and the amount of Fe^{3+} that is present. The work was presented in Delaney et al. (1998) and Dyar et al., 1998a, b; 1999; 2001a, b, c; and 2002b, c).
2. Proper interpretation of pre-edge features and their relationship to $\text{Fe}^{3+}/\Sigma\text{Fe}$ requires an understanding of their causes. In order to curve-fit the pre-edge of each spectrum, a model must be selected to determine how many components are present. Fundamentally, Fe K edge absorptions result from $1s \rightarrow 3d$ transitions enhanced by $4p$ mixing into the $3d$ orbitals. The number of transitions present (i.e., the strong field many-electron states) can be modeled for the $d^{(n+1)}$ excited state, assuming that the dominant effect of the $1s$ core hole is an increase in potential because it is spherically symmetrical (Westre et al., 1997). This $1s$ hole is so close to the nucleus that the outer orbitals see a configuration equivalent to that of the next highest ion on the periodic chart, with a fully occupied $1s$ shell. So, the final state of the ion, rather than having an atomic number of Z with a $1s$ hole, is instead best approximated by that of a different nucleus with atomic number $Z+1$ (Shulman et al. 1976; Calas and Petiau 1983). Thus, XANES spectra will show the energy levels predicted by the optical spectra for these $Z+1$ states.

Over the past several years, we have worked with George Rossman at Caltech to encourage optical studies of Co spectra of olivine and pyroxene that we need to understand XANES pre-edge spectra of those minerals; the first of these have now been published (Rossman and Taran, 2001). So we now have much of the analog Co spectra we need to interpret our XANES results.

3. In order to relate the optical spectra directly to XANES spectra, we needed XANES spectra acquired on oriented single crystals so that optical and XANES spectra at the same optical orientations could be compared. First, we had to invent a new method for orienting the samples and making these analyses on the microbeam synchrotron (described in Dyar et al., 2002b, c) and then begin to examine the effects of orientation on our $\text{Fe}^{3+}/\Sigma\text{Fe}$ results (Gunter et al., 2002).

This led to a set of extremely tricky experiments during the summers of 2001 and 2002 to acquire polarized microXANES spectra oriented along the optical orientation directions of end member Fe^{2+} and Fe^{3+} silicates (Dyar et al., 2002b, c; and 2003). We have learned that orientation effects contribute the majority of the analytical error in determinations of $\text{Fe}^{3+}/\Sigma\text{Fe}$ by the synchrotron micro-XANES method, and that the magnitude of this error varies according to mineral group (and crystal symmetry).

Task 5. Relating Fe^{3+} contents of phases to f_{O_2}

It is one thing to measure Fe^{3+} in a glass or minerals, but what we really want to know is the oxygen fugacity under which the rock formed. Although the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of rocks has been used frequently as an informal index of their f_{O_2} , the ratio is not a simple function of oxygen fugacity in most rocks, because mineral reactions, which depend on mineral compositions, control f_{O_2} , and where $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios depend on the abundances of phases in the rock (Frost, 1991). The matrix of most volcanic rocks records the final oxygen fugacity of the magma after the removal of previously crystallized phases, and at the eruption temperature. The oxygen fugacity of magmas along their crystallization paths has typically been obtained from the composition of coexisting iron-titanium oxides (Buddington and Lindsley, 1964; Ghiorso and Sack, 1991) but again, it can be difficult to determine where in the crystallization sequence the oxides grew, and identifying pairs in equilibrium is not always straightforward. Zoning in $\text{Fe}^{3+}/\text{Fe}^{2+}$ in pyroxene (Delaney and Dyar, 2002), amphibole (Dyar, work in progress), and feldspar crystals (Cartwright et al., 2000; Cartwright, 2002); thermodynamic modeling of melts and coexisting mineral assemblages (Ghiorso and Carmichael, 1985; Carmichael and Ghiorso, 1986); as well as common sense, all suggest that oxygen fugacity changes during the liquid line of descent of a magma, as a function of temperature and type and abundance of crystallizing phases. Thus, it is desirable to devise methods to quantify oxygen fugacity in all types of igneous rocks, even when coexisting iron-titanium oxides are not present or when petrogenetic relationships to them are not obvious (as is the case for many of the martian meteorites; c.f. Delaney and Dyar, 2002).

A first step toward this goal was made over the last year through our work with Molly McCanta, who was a graduate student working with Mac Rutherford at Brown University. The goal of McCanta's project was to relate the Fe^{3+} contents of coexisting glasses and pyroxenes to f_{O_2} . McCanta et al. (2003) reported Fe^{3+} results from a sequence of controlled f_{O_2} experiments on a synthetic basaltic shergottite starting composition, crystallizing low-Ca pyroxene. We also made Fe^{3+} measurements on a pre-existing suite of experimental charges of QUE analogs made and generously lent to us by Gordon McKay, in which augite was on the liquidus. $\text{Fe}^{3+}/\Sigma\text{Fe}$ contents of pyroxenes (pigeonite and augite) and coexisting glasses were characterized using synchrotron microXANES. Finally, McCanta ran a series of glass-only experiments for a cross comparison with Mössbauer spectroscopy, synchrotron micro-XANES, and wet chemistry (Figure 4). Results show a systematic increase in Fe^{3+} contents at high f_{O_2} 's, and excellent agreement between the various analytical techniques. This project was written up and accepted for publication in the *American Mineralogist* in 2004 (McCanta et al., 2004).

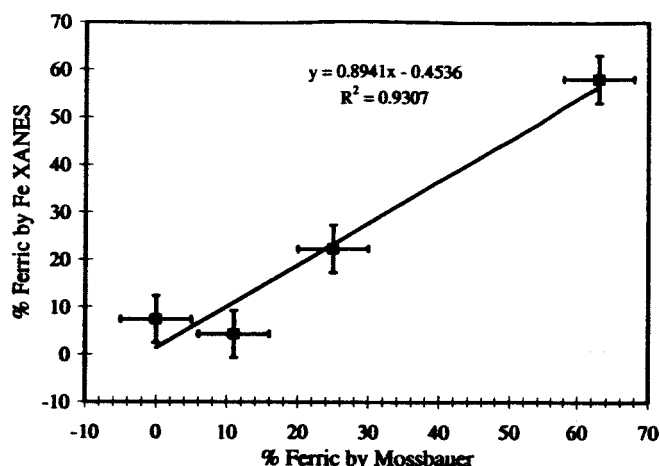


Figure 4. Comparison of Mössbauer and synchrotron micro-XANES results on shergottite glass equilibrated at variable f_{O_2} 's. The two methods show excellent agreement. Preliminary results of wet chemical analysis of these glasses also concurs with these data, validating the consistency of all three methods and showing the potential usefulness of the new XANES technique.

Task 6. Hydrogen and Fe^{3+} in SNC amphibole

The P.I. has long experience in the bulk and micro-analysis of amphiboles (e.g. Dyar et al., 1992; 1993; 2000a). From this, we predict that we will find an inverse relationship between H and Fe^{3+} in martian amphiboles, similar to what has been observed for mantle amphiboles. To examine this relationship, we are currently collaborating with Michelle Minitti in the study of the effects of shock on H and Fe^{3+} in amphibole. As part of her Ph.D. thesis work at Brown, Minitti prepared a series of variably-shocked amphiboles in order to study their H variation by SIMS (Minitti, 2001; Minitti et al., 1999). Using synchrotron micro-XANES, we analyzed $Fe^{3+}/\Sigma Fe$ in same grain mounts (in some cases, in the same locations) that Minitti used for her H analyses. No conclusions could be drawn from the results, in part because individual grains showed widely variable H and Fe^{3+} contents, suggesting that shock effects were heterogeneous.

Minitti has now started over on this project using better-controlled shock conditions and the 20 mm powder gun in the laboratory of Dr. T. Ahrens at Caltech, as well as our better-characterized samples as starting materials. For this new project, we selected a suite of large amphibole crystals from Dyar's collections (covering a range of *known* starting Fe^{3+} and H contents) for shock experiments under controlled conditions (roughly 20-35 GPa and varying atmospheres). The first experiments took place in the fall of 2001, and were presented at LPSC 2003 (Minitti et al., 2003). We have just finished Mössbauer analyses of these samples, and expect to report the results at LPSC in 2005.

Task 7. Quantify changes in Fe^{3+} and H contents of martian-analog minerals with shock

Interpretation of data from the previous Tasks depends on the assumption that shock effects do not change either Fe^{3+} and H. This assumption has barely been tested; a few previous workers (e.g. Bauer 1979; Ostertag and Stöffler, 1982) have suggested that shock followed by thermal annealing can result in oxidation of olivine. As reported in Therkelsen et al. (2002a, b), over the past two years we undertook a pilot project to test the relationship, if any, between shock and oxidation/reduction and hydrogenation/dehydrogenation. Samples were analyzed for $Fe^{3+}/\Sigma Fe$ using synchrotron micro-XANES spectroscopy.

Results of this senior thesis project (Therkelsen, 2002) and subsequent work (Delaney et al., 2003) were mixed. Major element compositions of feldspar, pyroxene, and olivine remained unchanged as a function of increasing shock pressure, suggesting that the temperatures involved were not high enough to either volatilize Na or diffuse other major elements. The FeO content of the feldspar is roughly constant over the range of pressures studied, so there is no evidence for the presence of a mafic component

(resulting from melting of proximal olivine or pyroxene) that might indicate the presence of shock melt glass.

The *percentage* of total Fe present as Fe^{3+} changed little with increasing shock pressures, though the effect is different for different minerals because of their composition and steric constraints. There is some indication of oxidation of olivine and feldspar with progressive amounts of shock, but the amount of change is within the error bars for the technique. Data collection and interpretation were frustrated by the heterogeneity of the starting materials and the presence of alteration products heterogeneously distributed in them. Furthermore, the pyroxenes in both starting rocks were exsolved to varying degrees. We did not find any of the oxidized brown olivines described by Bauer (1979) and Ostertag and Stöffler (1982), probably because of the lack of thermal annealing.

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